

Development Glass Ceramics from Blast Furnace Slag

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF**

Bachelor in technology

In

Ceramic Engineering

BY

Sumit Kumar Aman

Roll no.-110CR0539

Under the guidance of

Prof. Sumit Kumar Pal



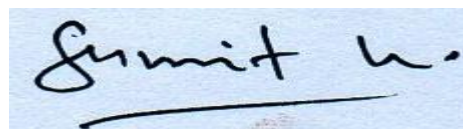
Department of Ceramic Engineering

National Institute of Technology, Rourkela

2014

DECLARATION

I am **Sumit Kumar Aman**, a student of Department of Ceramic Engineering, **National Institute of Technology Rourkela** bearing **Roll Number-110CR0539** hereby certify that my B.tech Project Report entitled “**Development of Glass Ceramic from Blast furnace Slag**”, under the guidance of **Prof. Sumit Kumar Pal** at **National Institute of Technology, Rourkela**. This is a record of bona fide work carried out by me and the results presented in the Project Report have not copied from any source. The results presented in this Project Record not have submitted to any other University or institute for the award of any other certificate or degree.

A handwritten signature in black ink on a light blue background. The signature appears to be 'Sumit K.' with a horizontal line underneath.

ROURKELA

SUMIT KUMAR AMAN

DATE: 12/05/2014

DEPARTMENT OF CERAMIC ENGINEERING

NIT, ROURKELA



NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA CERTIFICATE

This is to certify that the Project Report entitled “**Development of Glass-Ceramics from blast furnace slag**”, being submitted by **Mr. Sumit Kumar Aman**, Department of Ceramic Engineering, National Institute of Technology Rourkela, under the requirement for the Degree of Bachelor of Technology in **Ceramic Engineering** is a record of bona fide work carried out by him, under my guidance and supervision. The results enclosed in this report have been verified and found to be satisfactory.

The results presented in this Project Report have not been submitted to any other University or Institute for the Award of any other certificate or degree.

ROURKELA

DATE: 12/05/2014

Dr. Sumit Kumar Pal

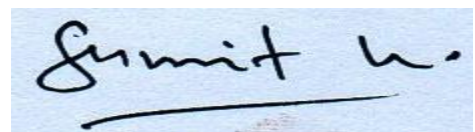
Assistant Professor

Department of Ceramic Engineering

NIT Rourkela, ODISHA

ACKNOWLEDGMENT

With deep respect, I avail this opportunity to express my gratitude to Dr. Sumit Kumar Pal, Assistant Professor, National Institute of Technology, Rourkela for his inspiration and guidance and valuable suggestion throughout this research work. It would have been impossible on my part to come out with this project report without him. I would like to express my gratitude to Dr. S. Pratihara (HOD), Ceramic Engineering for permitting to carry out my project. I would like to take this opportunity to thank all the faculty members of Ceramic engineering Department namely Dr. Jages Bera, Dr. B.B. Nayak, Dr. D. Sarkar, Mr A. Choudhury, Dr. S. Behera , Dr. R. Mazumder, Dr. R. Sarkar, Dr. S. Das gupta, and Dr. S. Bhattacharyya. I would also take this opportunity to express my gratitude to the non-teaching staff Bapi sir, Mr Arvind Kumar, and Ezhil Venuswaran (PhD. Scholars) for the help and support in carrying out experiments and providing every sort of help possible.

A handwritten signature in black ink on a light blue background. The signature appears to read 'Sumit K.' with a horizontal line underneath.

SUMIT KUMAR AMAN

DEPARTMENT OF CERAMIC ENGINEERING

NIT ROURKELA

Contents

Abstract.....	7
CHAPTER 1 : INTRODUCTION	
1.1 Introduction.....	9
CHAPTER 2 : LITERATURE REVIEW	
2.1 Literature Review.....	12
CHAPTER 3 : EXPERIMENTAL PROCEDURE	
3.1 Chemical analysis	16
3.2 Batch preparation.....	17
3.3 Melting of batch.....	18
3.4 Bulk density.....	18
3.5 Three point Bending	19
3.6 Vickers hardness.....	20
3.7 Compressive strength (CCS).....	21
3.8 FESEM.....	23
CHAPTER 4: RESULT AND DISCUSSION	
4.1 Determination of melting temperature.....	25

4.2 Preparation of glass ceramics.....	26
4.3 Hardness of glass.....	29
4.4 Bulk density of glass sample.....	30
4.5 Flexural strength of glass.....	31
4.6 Hardness of glass ceramics.....	32
4.7 Bulk density of glass ceramic.....	33
4.8 Compressive strength of glass ceramics.....	35
4.9 Dilatometer test of glass ceramic.....	36
4.10 Microstructure observation by FESEM.....	37
 CHAPTER 5: CONCLUSION	
5.1 Conclusion.....	39
REFERENCE.....	40

Abstract

Glass ceramics have a wide range of applications in today's world. The production of glass ceramics from industrial waste such as fly ash, red mud, blast furnace slag gaining more importance now a days because of their availability and low cost. In the present work an attempt has been made to produce glass ceramic with high alumina content using blast furnace slag. Generally alumina is very difficult to melt. To produce base glass for glass ceramic from blast furnace slag, an additional low melting phase which aid in dissolving the alumina can be provided by blast furnace slag. Blast furnace slag is generally produced at the temperature range 1300°C to 1400°C. High alumina content glass with alumina percentage as high as 30% (more alumina content in E-glass) requires melting temperature as high as 1600°C. Therefore using blast furnace slag as one of the main constituents can help in reducing the melting temperature of the precursor glass prior to glass ceramic production. More over high alumina content in the glass as well as in glass ceramic can enhance different physical properties, like high mechanical strength, high durability, low thermal expansion co efficient which are very suitable for cooktop application. In the present work an attempt has been made glass ceramics from blast furnace with alumina content 32% . Glasses are melted at 1400°C. For glass ceramic production glasses are heat treated at 750°C, 850°C and 950°C. Glass ceramic products are characterize by Vickers Hardness, Bulk density measurement, Flexural strength , Compressive strength , Dilatometer test and FESEM.

CHAPTER: 1

INTRODUCTION

INTRODUCTION

The industrial waste is one of the major environmental problem worldwide. Blast furnace slag is waste of iron and steel making plant[1]. In various countries, the drawback of number of dumping landfill sites and the general discarding methods has rendered the environment unfriendly[3]. To reduce this problem waste must be re used or recycled which is produced by industry. So that raw material cost will be minimize as well as for environment protection[2]. Using blast furnace slag as raw material for precursor glass prior to glass ceramization can be a effective way to recycle the blast furnace slag..

Glass ceramics are formed by controlled heat treatment, with parent Glass along with other desirable composition. The glass is first melt quenched then it is heat treated with controlled heating rate in various time interval. With controlled heat treatment nucleation takes place homogeneously followed by growth mechanism. Through this method with controlled crystallization various property improvement can be achieved.

The blast furnace slag formed in the process of formation of pig iron from iron ore[6], it is obtained by water quenching or air quenching ,Due to rapid cooling blast furnace slag mostly found in glassy phase and due to water quenching they are eventually form in granular mode. And it is easy to make in a powder form. Generally blast furnace slag contains residue of coke, limestone's fluxes or serpentine and other materials like mixture of metal oxides and silicon dioxide [2]. If the molten slag cooled quickly in high pressure water zone, fine grain of slag can be formed. Generally the composition of blast furnace slag contains SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 in major amount. Since this is a slag so there can be anything in the composition of blast

furnace slag that may be CaF_2 , MnO , Na_2O , TiO_2 . Properties of final product may vary with the slag composition because slag generated from different industry may be different from each other. Dissimilar procedures of Slag products vary according to the technique use in cooling the molted slag.

In the present work an attempt has been made to produce glass ceramic from blast furnace slag with high alumina content. High alumina content in glass ceramic can improve different properties in glass ceramic. With high alumina content a glass ceramic is expect to have high mechanical strength, high corrosion resistance and low thermal expansion coefficient, which will be very suitable for cook-top application.

CHAPTER: 2

LITERATURE REVIEW

Literature review

Low cost Glass ceramics from molted Blast furnace slag have been studies by *Zhao et.al. [1]*, wherein as a raw material used molten blast furnace slag and silica(SiO_2), low energy consumption as compare to conventional method because of use of molten slag. In this high ratio of blast furnace slag approximate 90%. The effect of CaF_2 (microstructure) studied by XRD, DSC and SEM, and bending strength of measured by Three point bending method. The bending strength of the glass–ceramics was about 45.8 MPa. If CaF_2 add then it's strength increased greatly to 120 Mpa.

Glass–ceramics made from blast-furnace slag by a conventional sintering process. *Hongyu Liu et.al.[2]* studied the properties of glass ceramics which is made by blast furnace slag and potash feldspar as additives. It shows that 5 wt% feldspar improve the sintering properties, And 5.2 GPa of micro hardness and bending strength was greater than 85 MPa as well as absorption of water below 0.14% obtained.

Blast furnace slag converts into Glass-Ceramics materials *Francis [3]* studied SEM , XRD and DTA analysis. The crystalline phases was found as gehlenite, diopside pyroxene and barium aluminium silicate. The maximum density found at 900 °C. At temperature of 1050 °C acicular and dendritic morphology have been identified. A slight variation in peak crystallization temperature with particle size indicated a bulk crystallization mechanism.

The effect of composition of glass ceramics on crystallization behavior made by blast furnace Slag *Mihailova et.al [4]* studied on the composition blast furnace slag 68-80 wt% , kaolin, Al_2O_3 And TiO_2 . Glass ceramics made by sintering process of glass powder at 1000 °C. The crystalline phases was identified to be anorthite melilite, anorthite and pyroxene. The ratio between

crystalline phases depends on chemical composition of the glass.

SiO₂-CaO-Na₂O-MgO based glass ceramics sintering behaviour on adding calcium fluoride

Mirhadi et.al. [5] reported when increases content of CaF₂, decreases the crystallization

Temperature of glass and also decreases the strength of crystallization peak temperature. Till

Addition of 6.0 mol% of CaF₂ sinterability improved. This sample shows maximum density by sintering at 950 °C.

Phase separation mechanism in blast furnace slag glass phase **Yu et.al. [6]** reported that A necessity of development for the phase separation of the blast furnace slag glass phase was this the composition of blast furnace slag detects in the existing point region of melilite and any silicate with Q⁰ units in CaO-MgO-Al₂O₃-SiO₂ system. One with chemical composition of larger ratio of (CaO+MgO)/(SiO₂+Al₂O₃) would be more encouraging to meet the condition. Melilite was categorized as sorosilicate, but it was a layer structure with high DOP for the special melilite units, a 5- membered ring made of Si₂O₇ + MgO₄ or (Si,Al)₂O₇ + AlO₄, this plays the lead role of the phase separation.

Volume Nucleation of crystal based on blast furnace slag in glass **Sycheva et.al.[7]** studied that by blending metallurgical slag with silicon dioxide the nucleation of crystals in glass obtained. It was shown that the first crystalline phase in a volume crystallizing glass was perovskite (CaO · SiO₂); in this phase a nucleation of the main phase occurs: melilite (solid solution of gehlinit 2CaO · Al₂O₃ · SiO₂ in akermanite 2CaO · MgO · 2SiO₂).

G.A. Khater [8] observed that the presence of Cr₂O₃, TiO₂, CaF₂ and LiF enhance the crystallizability of the glass. Cr₂O₃ and TiO₂ are better promoter for homogeneous nucleation as well as for the formation of extremely fine-grained microstructure of aluminous pyroxene and magnetite than LiF and CaF₂.

Zhong-jie Wang et. al[9] studied the crystallization behavior of glass ceramic formed by mixture of BF lag nickel slag and quartz sand with the help of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM) in his paper. When the glass is heated up to 700 °C then a large number of tiny spherical crystals forms and the radial crystals form when the glass is heated up to 820 °C. The crystallization temperature is found to be 860 °C. Crystals of diopside ($\text{CaMg}(\text{Si,Al,Fe})_2\text{O}_6$) and hedenbergite ($\text{CaFe}(\text{Si,Al,Fe})_2\text{O}_6$) are observed as final phases and the activation energy of crystallization is found to be about 201.28 kJ/mol.

CHAPTER: 3

EXPERIMENTAL

PROCEDURE

3.1 Chemical analysis

Taken 0.5203 gm of sample (Blast furnace slag) in platinum crucible and 10 gm of Na_2CO_3 and added few bit NaOH . Mixed it properly and fuse the mass at 1000°C for 1 hrs. cool it down transfer the mass in 100 cc HCL taken in a 250 ml beaker. Kept the beaker at hot plate for overnight till complete drying (Beaking) then add 50cc 1:1 HCL and warm it and after this filtrate the mass through WHATMAN 540 filter paper, collect the filtrate 1 in a 250ml volumetric flask. Take the residue in a pre-weighted crucible fire at 1000°C for 1 hrs. residue is reported as silica.

Determination of Mixed oxide (Fe_2O_3 and Al_2O_3):

Make the volume of a filtrate 1 upto the mark taken 50cc of filtrate 1 in a 250 ml beaker added few drops of Methyl red indicator (color red in acidic medium), added ACC buffer till medium is alkaline (yellowish green color) warm it and filtrate through WHATMAN 541 filter paper collect filtrate 2 in a 250cc volumetric flask fire the residue at 1150°C for 1 hrs. report the residue as Mixed oxide.

Determination of Fe_2O_3 :

Taken 10ml of filtrate 1 in 250ml conical flask added 10cc of ammonium thiocyanate solution color become blood red. Filtrate it against standard mercurous Nitrate solution with vigorous till color less end point. Calculate the amount of iron oxide from $\text{Ag}_2(\text{NO}_3)$ consumed report the difference from the mixed oxide as Al_2O_3 .

Determination of CaO and MgO :

Make up the volume of filtrate 2 and take 10cc of filtrate 2 in 250ml conical flask add 10cc AAC buffer and a pinch of Eriochrome black T (EBT) indicator color become wine red titrate it

standard EDTA solution (0.01M) till sky blue end point. Calculate the amount of CaO and MgO from EDTA consumed.

Determination of CaO:

Taken 10ml of filtrate of filtrate in conical flask added NaOH solution (10%) and add a pinch of P&R indicator color become light violet titrate it against standard EDTA. Report CaO from the volume of EDTA consumed. . The chemical composition of blast furnace slag after analysis composition was found as:

SiO₂ (wt%)	Al₂O₃ (wt%)	CaO (wt%)	MgO (wt%)	Fe₂O₃ (wt%)
35.29	27.58	26.94	8.71	1.15

Table-3.1 Composition of blast furnace slag

3.2 Batch preparation

The project started with the batch calculation and finding the chemical composition of blast furnace slag. Blast furnace slag (provided by RSP Rourkela) was milled in Pulverizer mill for about 1 hours. Blast furnace slag converts into fine powder .Batch composition fixed as:

	B F SLAG	Al₂O₃	CaF₂	B₂O₃	TiO₂
Batch-1(Wt%)	80	10	5	4	1
Batch-2(Wt%)	80	10	5	4.5	0.5

Table-3.2 Batch composition

As fixed the batch composition, two batches were made in proper manner and mixed the batch perfectly.

Final composition of glass-ceramics:

	SiO ₂	Al ₂ O ₃	CaO	MgO	CaF ₂	Fe ₂ O ₃	B ₂ O ₃	TiO ₂
Batch-1(wt%)	28.23	32.06	21.55	6.97	5	0.92	4	1
Batch-2(wt%)	28.23	32.06	21.55	6.96	5	0.92	4.5	0.5

Table-3.3 composition of glass ceramics

3.3 Melting of batch

After fixing the melting temperature taken both batch separately in silimanite crucible and goes for melting at temperature of 1400°C soaking time was 1 hours. And heating rate was on control mode. On completion of scheduled heating pored that melt on graphite plate and annealing for 3 hours. Two glass plate made from the above mentioned method and named as batch-1 and batch-2.

3.4 Bulk density

Bulk Density (B.D) is defined as the material present in a given volume that is, it is the ratio of the mass of a material to its bulk volume, i.e. the volume of the given material plus all the pores within it. An increase in bulk density of a given glass ceramic increases its volume stability, its heat capacity, its mechanical and thermomechanical property as well as resistance to corrosion.

It is measured by Evacuation method. First of all, the made glass and glass ceramic samples is weighed and noted down. This weight is dry weight (D). The dry specimen is placed in empty desiccator and then is evacuated to remove the trapped air. Now samples are suspended in

immersion liquid and weighed. This is suspended weight(S). Then the test sample is dried using a blotting paper. After which soaked weight (W) is calculated.

Calculation:

$$\text{B.D.} = [\text{Dry Weight} / (\text{Soaked Weight} - \text{Suspended Weight})]$$

3.5 Three point Bending or Flexural strength of glass

Three point bending or flexural strength is also known as Modulus of Rupture, it is a mechanical parameter for measuring strength of material. It is describe as a material ability to resist deformation under load.

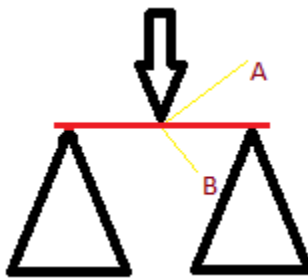


Figure-3.7 Beam of material under bending. A shows compression and B shows tension)

Specimen measuring and cut from the desired glass shape and placed it on the bearing edges of the machine and then start apply uniformly rate load at middle of the sample after that the load on which the sample breaks is noted and M O R of the sample is calculated from the equation:

$$\text{M.O.R.} = 3WL/2bt^2$$

Where W – applied load (N)

 L – Distance between two bearing edges (cm)

 b – Width of sample (cm)

t – Thickness of sample (cm).

3.6 Vickers hardness

Hardness is the property of a material that allows resistance to plastic deformation, by penetration. Hardness may also refer to resistance to bending, rubbing, scratch or cutting.

In Vickers hardness test method, the test material is indented with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136 degrees between opposite faces and a load of 0.3 Kgf is applied. The load was applied for 4 seconds. The two diagonals of the indentation in the surface of the material after removal of the load are measured with a microscope attached to testing machine and their average is calculated. The area of the indentation is calculated. The Vickers hardness is obtained by dividing the kgf load by the square mm area of indentation.



3.8 Vickers hardness testing machine

Calculation:

$$HV = \frac{2.854F}{\text{area of indentation}(d^2)}$$

Where,

F=load

d= avg. of indentation

3.7 Compressive strength (CCS)

The compressive strength is the maximum compressive stress a material is capable of withstanding without fracture. Brittle materials fracture during testing and have a definite compressive strength value. The compressive strength of ductile materials is determined by their degree of distortion during testing.

The compressive strength testing is performed in Universal Testing Machine (UTM). First dimension of the test piece is measured at three different places along its height or length to determine the average cross-section area. The specimen is placed centrally between the two compressions plates, such that the center of moving head is vertically above the center of specimen then Load is applied on the specimen by moving the movable head. The load and corresponding contraction are measured at different intervals by the computer attached to the UTM. Load is applied until the specimen fails. The load at which specimen fails is noted and this

is maximum force (F_{max}) and the surface area of the base is calculated and then compressive strength can be calculated.



Fig. 3.9 Universal Testing Machine (UTM)

Calculation:

$$\text{Compressive Strength} = \frac{F_{max}}{L_1 \times L_2}$$

Where, F_{max} is the force applied for failure and $L_1 \times L_2$ is the area of the base of specimen.

3.8 Microstructure observation by FESEM

The FESEM is generally used to analyze the grain-shape, grain-size, packing of grains, grain boundary, pore shape and size new phases etc. The prepared samples have been cut into small pieces. The surface of testing specimen is polished by three consecutive polishing (6 μ m, 3 μ m, and 1 μ m cloth) using diamond suspension spray. Ultra cleaning of samples is performed after each polishing. After that carbon coating has been done and loaded into the sample holders and FESEM analysis has been performed.

CHAPTER: 4

RESULTS

AND

DISCUSSION

4.1 Determination of melting temperature of precursor glass

Temperature at which the materials changes solid to liquid stage is known as melting temperature. To find melting temperature of the glass batch, both batches named as batch-1 and batch-2 with composition as mentioned in table-2. After making two batches, made some piece plate through hydraulic pressing machine and using die-punch. When plate made all the sample put into furnace one by one at different temperature and different soaking time and observe,







Temp. (°C)	Batch-1	Batch-2
1100 (15 min.)		
1200 (15 min.)		
1300 (15 min.)		

Figure-4.1 At temperature 1100,1200,1300 °C

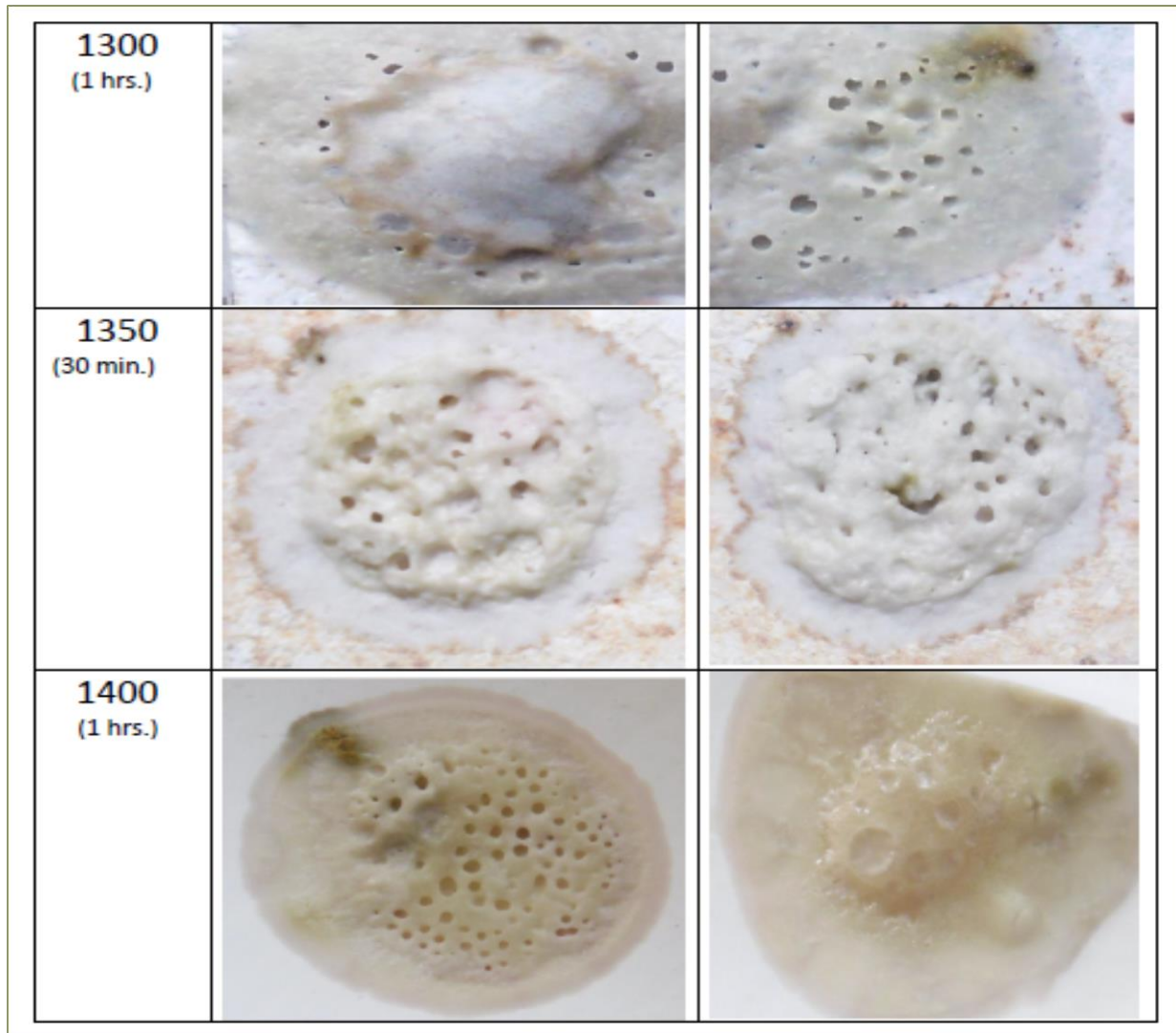


Figure-4.2 At temperature 1300, 1350, 1400°C

As shown in figure 4.1, at 1100°C sintering occurs but it doesn't form any molten phase, while at 1200°C some phases softened and eutectics started forming. At 1300°C partial melting occurs and eutectic formation is complete. At 1300°C, the soaking time was increased and due to that some more melting phases formed and some bubbles start coming out from the batch. At 1350°C the batch doesn't melt completely because of the presence of high alumina in the compositions but bubble formation continues. The bubbles try to come out but due to the high viscosity of melt they do not come out completely. At 1400°C batch melts completely and form

glassy phase. The bubbles escape completely from the melt. This helps in concluding that melting point of batches was 1400°C. Another observation that was made was that the color of the batches changed from white to brownish during the melting process. This was due to the effect of the impurities present in the blast furnace slag used. Since 80% slag was used in the composition, the colour change was significant.

4.2 Glass-ceramization

To prepare the glass ceramic as prepared glasses were heat treated Preparation at the temperature 750 °C, 850 °C, 950°C with a soaking of 4 hours. There significant changes in appearance observe after every heat treatment.



Fig.-4.3 Glass reheated at 750 °C

It has been observed that after heat treatment at 750°C for 4 hours there is change in appearance in the glass samples. Glass has lost its transparency and it became translucent. The translucency in the glass samples are due to scattering of light from the glass samples. So it is evident that after heat treatment there is nucleation took place homogeneously due to presence of TiO₂ which

were mixed homogeneously inside the glassy matrix. TiO_2 worked as nucleating agent . The creation of new interfaces inside the glassy matrix provides sites for scattering of light . Hence it can be concluded that nucleation has been taken place which is followed by growth. But the growth is not completed as the temperature is low which offers high viscosity to the moving species creating kinetic barrier towards growth.



Fig.-4.4 Glass reheated at 850 °C

It has been observed that after heat treatment at 850°C for 4 hours there is change in appearance gain in the glass samples. The glass has lost its transparency completely and it is also transforming to an opaque body. As the temperature has been increased therefore, the viscosity of the glass matrix has been reduced which help in diffusion of different species inside the glassy matrix. As the diffusion barrier is low there are more number of atoms which leave the glassy phase and joins the crystalline phases. As it joins the crystalline phases different grain boundary formation takes place which provides site for light scattering. Therefore, the glassy body is slowly transforming to opaque appearance.

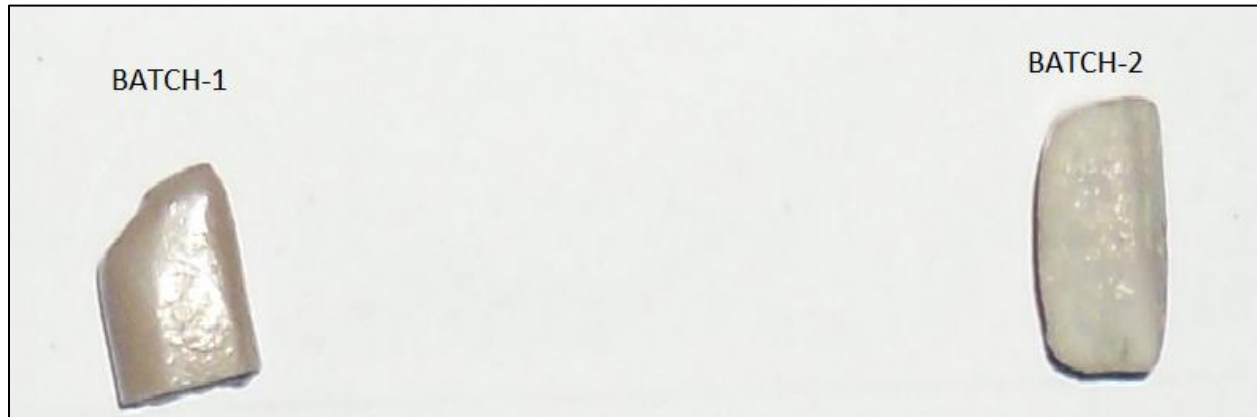


Fig.-4.5 Glass reheated at 950 °C

When the glass heat treated at 950oC for 4 hours, it has been observed that the glass has transformed into a opaque body. AT 950 oC there is very low kinetic and thermal barrier towards the diffusion. Homogeneous nucleation has been completed and growth mechanism has taken control over the matrix. Different alumina- silica phase has been precipitated as crystals. The grain boundaries associated with crystalline phase has been formed which has been distributed thoroughly inside the glassy matrix hence the glass sample is totally opaque.

4.3 Hardness of glass

Hardness of the glass surface was measured using Vicker's hardness testing machine and the following data was found:

Hardness of batch-1	693.8 Hv
Hardness of batch-2	582.0 Hv

Table 4.1 Hardness value of glass

It can be seen that batch 1, which is having a higher amount of TiO_2 , has a higher strength. Thus the effect of nucleating agent can be seen. The increased nucleation, strengthens the structure and increases hardness. As there is more number of nucleating site available therefore, it lead to more crystallization. As the crystallization has been extended to surface therefore, it can be summarized that alumina reach phase has been precipitated throughout the matrix. Alumina silica phase offers high hardness. Therefore, there is increase in surface hardness value as there are more crystals site available on the surface. On the other hand, batch 2, having a lower TiO_2 content has a lower strength, although the amount of glass former B_2O_3 is more.

4.4 Bulk density of glass sample

Bulk density was measured by Archimedes principle and the data found:

	D(g)	S(g)	W(g)	$\text{BD}=\text{D}/\text{W}-\text{S}(\text{g/cc})$
Batch-1	4.1719	2.692	4.177	2.8142
Batch-2	4.2935	2.765	4.290	2.8154

Table 4.2 bulk density of glass

The data shows that the density almost remains similar in both batches. The change in the percentage of nucleating agent and glass former, if less than 1%, doesn't affect the density much. Batch, although, has a slightly higher density due a higher B_2O_3 content.

4.5 Flexural strength of glass

The flexural strength has been calculated for each batch using the following formula:

$$\text{M.O.R.} = 3WL/2bt^2$$

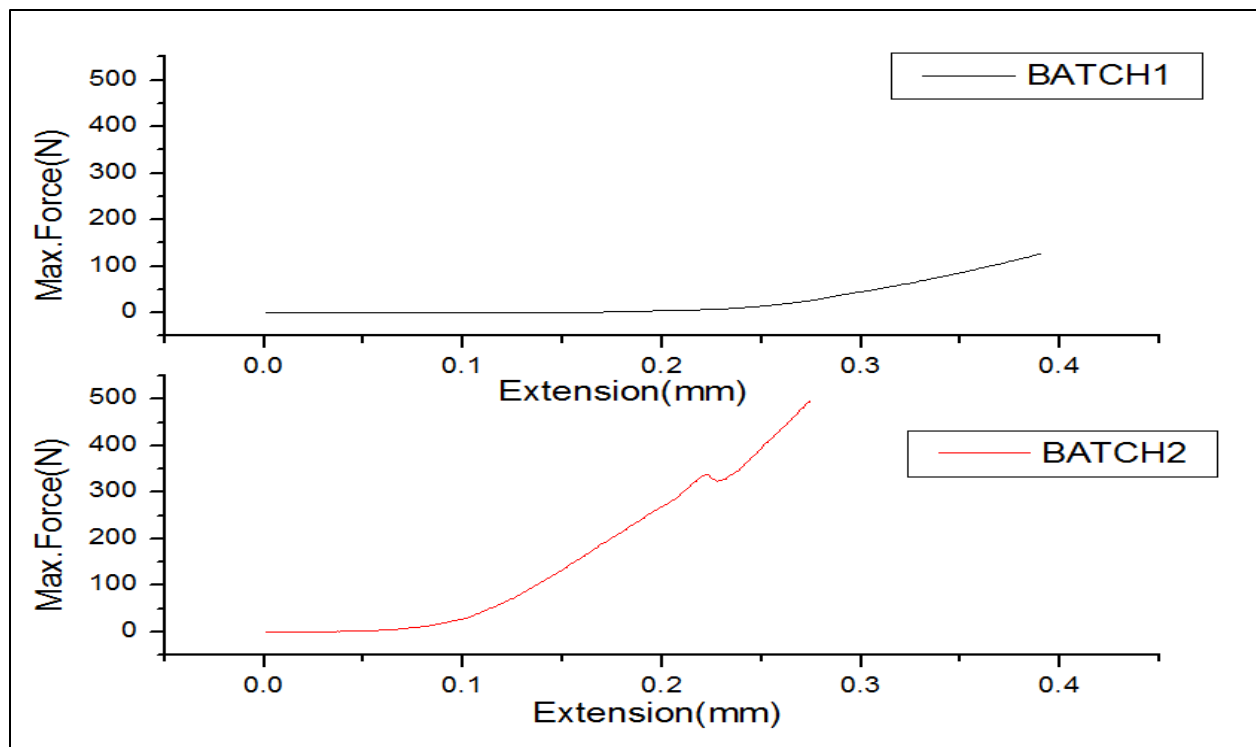


Fig. 4.6 Displacement at breaking point vs max. load

For batch 1, the flexural strength was found to be 101.446 MPa at a maximum extension of 0.3910 mm. For batch 2, the flexural strength was found to be 91.8 MPa at a maximum extension of 0.2750 mm. A higher amount of nucleating agent TiO_2 in batch 1 leads to more crystallization and thus a higher strength. Also, the brittleness due to the glassy phase is lower and a greater extension can be seen. As there is more site for nucleation available therefore, crystallization is more. Crystal phases are embedded in glassy matrix which offer high resistance

towards the crack propagation. Therefore, the glass ceramic which have more nucleating agent have more crystallization shows more flexural strength.

4.6 Hardness of glass ceramics:

Temperature (in °C)	Batch-1 Hardness (in Hv)	Batch-2 hardness (in Hv)
750	1574.6	1594.6
850	1571.65	1599.4
950	1599.05	1610.4

Table 4.3 hardness of glass ceramics

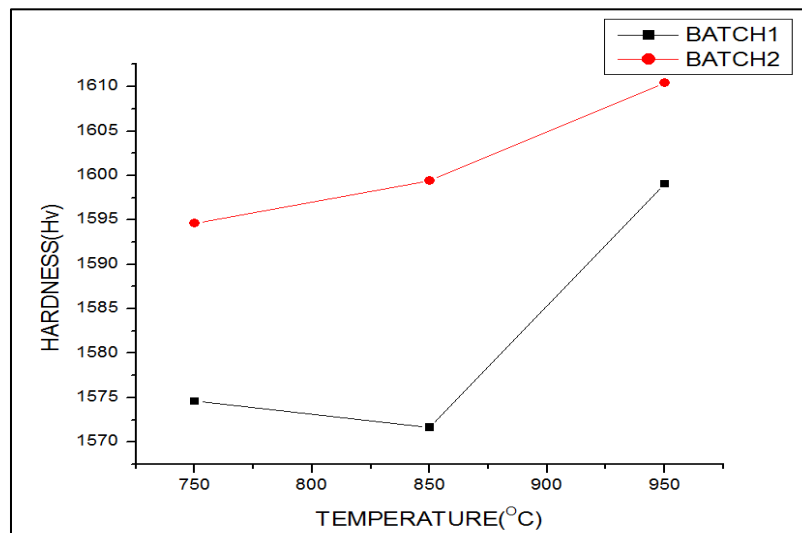


Fig. 4.7 (hardness vs temperature)

Hardness of the glass ceramic increases with increases the temperature in both the batch due to increasing the density and crystal formation in glass ceramics. At 750°C the melting is least,

hence, on cooling the crystallisation is not significant. Since the glass ceramic formation is minimal, the strength is lowest in this case. The same happens at 850°C but here the strength is higher due to higher crystalline phase formation. At 950°C, the strength is highest as the crystalline phase formation is the highest here.

4.7 Bulk density of glass ceramic

As the glass volume is fixed so nucleation and growth which took place inside the glassy matrix did not offer much towards the bulk density. The glassy matrix is generally consists of alumina silica. Alumina as well as silica present inside the glassy matrix as 4 coordination state. All Si is surrounded by 4 oxygen. Same can also be said for alumina. Alumina is also present in the 4 coordination state. As there is glassy phase therefore, it offers high specific volume than its corresponding crystalline phase. The high specific volume lead to high free volume inside the glassy phase. As there is nucleation and growth took place, therefore, these free volumes are getting occupied by crystallization. As there is no mass transport from outside, all mass transport are due to diffusion mechanism inside the glassy matrix, therefore there is no increase in mass as well as there is no increase in volume. Hence there is no significant change in bulk density.

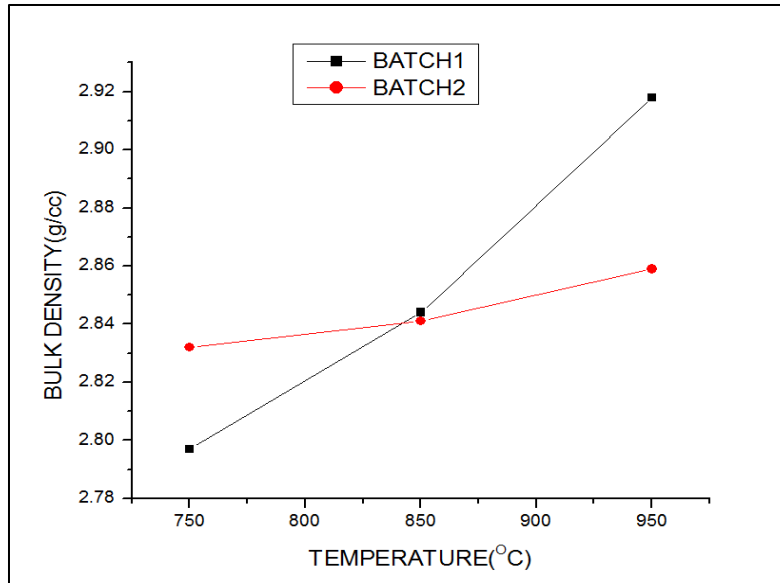


Fig. 4.8 (bulk density VS temperature)

As shown in graph, density increases slightly with increase in temperature, because with increase in temperature, volume decreases slightly but crystallization in the glass ceramic increases with temperature filling up the free volume. Since, mass is constant here, therefore density increases slightly. At 750°C density for batch-1 and batch-2 found 2.797 and 2.832 g/cc respectively. At 850°C density found very similar and at 950°C density for batch-1 and batch-2 found 2.918 and 2.852 g/cc respectively.

4.8 Compressive strength of glass ceramics

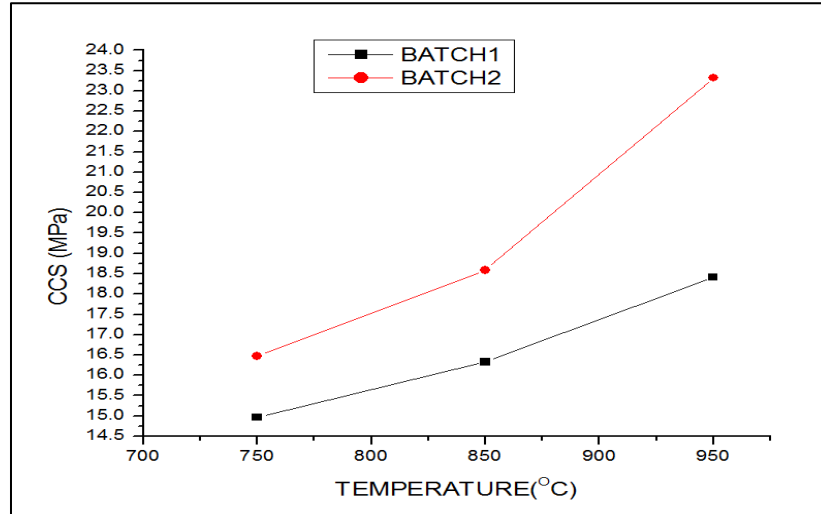


Fig. 4.9 (CCS vs temperature)

As shown in fig. 4.4 CCS value increases with increase the temperature because crystalline form increases with increases the temperature. At 750°C the melting is least, hence, on cooling the crystallisation is not significant. Since the glass ceramic formation is minimal, the strength is lowest in this case. The same happens at 850°C but here the strength is higher due to higher crystalline phase formation. At 950°C, the strength is highest as the crystalline phase formation is the highest here.

4.9 Dilatometer test of glass ceramic

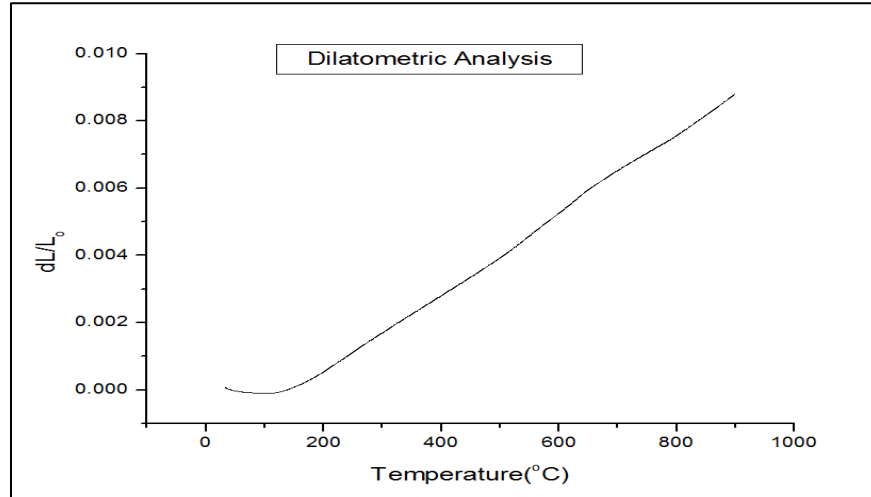


Fig. 4.10 (temperature vs dL/L_0)

Thermal expansion co-efficient= 8.028×10^{-6} /°C in the range of 400°C. So it can be used as cooktop. As there is high alumina content present in glass ceramic phases therefore it shows very less thermal expansion coefficient. The alumina in glassy matrix offer high viscosity at low temperature. So on heating the alumina phases cannot go inside the free volume. As there is also silica phase present inside the glassy matrix therefore, it offers low thermal expansion coefficient.

4.10 Microstructure observation by FESEM

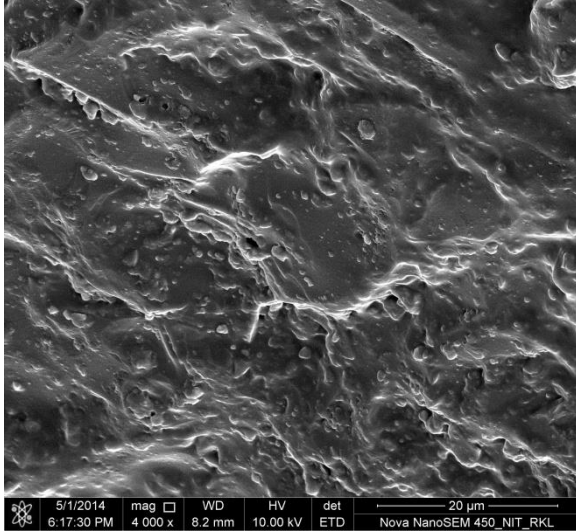


Fig.4.11 Glass ceramic fired at 850°C

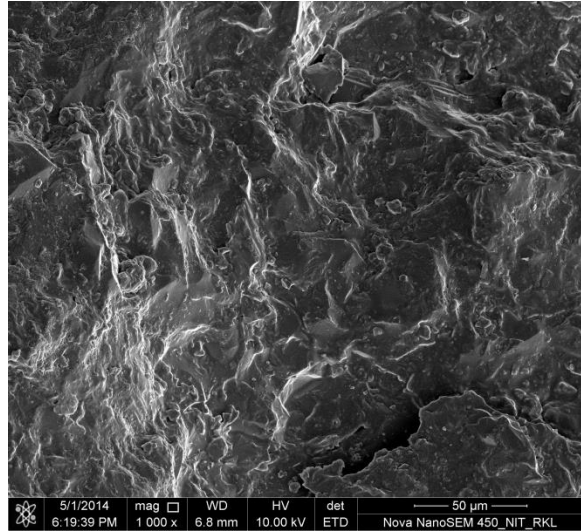


Fig.4.12 Glass ceramic fired at 950°C

From the microstructure it has been observed there are crystal phases embedded inside the glassy matrix. In sample heat treated at 850oC shows very tiny crystals embedded inside the glassy matrix. No porosity has been observed in the samples. IN the samples heat treated at 950oC , there is some crystal boundary seems to be visible. Similarly no porosity has been observed in this samples.

CHAPTER:5

CONCLUSION

5.1 Conclusion

It can be concluded that :

- Melting temperature for this composition was found about 1400°C with soaking time about 1hour.

	B F SLAG	Al₂O₃	CaF₂	B₂O₃	TiO₂
Batch-1(Wt%)	80	10	5	4	1
Batch-2(Wt%)	80	10	5	4.5	0.5

- Hardness of the glass ceramic increases with increases the temperature of heat treatment in both the batch.
- Density increases continuously with increase in temperature of heat treatment in both the compositions.
- CCS value increases with increase the temperature because crystalline form increases with increases the temperature.
- This glass-ceramics shows lower thermal expansion co-efficient. Thermal expansion co-efficient= 8.028×10^{-6} /°C in the range of 400°C. So it can be used as cooktop application.

REFERENCE

1. Yan Zhao, Dengfu Chen a, Yanyan Bi, Mujun Long. Preparation of low cost glass–ceramics from molten blast furnace slag , *Ceramics International* 38 (2012) ,pp.2495–2500
2. Hongyu Liu, Hongxia Lu , Deliang Chen, Hailong Wang, Hongliang Xu, Rui Zhang. Preparation and properties of glass–ceramics derived from blast-furnace slag by a ceramic-sintering process , *Ceramics International* 35 (2009), pp. 3181–3184
3. A.A. Francis. Conversion of blast furnace slag into new glass-ceramic material , *Journal of the European Ceramic Society* 24 (2004) pp. 2819–2824
4. I. K. Mihailova^{1,*}, P. R. Djambazki¹, D. Mehandjiev² . The effect of the composition on the crystallization behavior of sintered glass-ceramics from blast furnace slag , *Bulgarian Chemical Communications*, Volume 43, Number 2 2011, pp. 293–300
5. Bahman Mirhadi, Behzad Mehdikhani . Effect of calcium fluoride on sintering behaviour of SiO₂-CaO-Na₂O-MgO glass-ceramic system , *Processing and Application of Ceramics* 6 [3] (2012) ,pp.159–164
6. LI Yu¹, LIU XiaoMing, SUN HengHu & CANG DaQiang . Mechanism of phase separation in BFS (blast furnace slag) glass phase, *SCIENCE CHINA Technological Sciences* , January 2011 Vol.54 No.1: pp.105–109

7. G. A. Sycheva and I. G. Polyakova . Volume Nucleation of Crystals in Glass Based on BlastFurnace Slag , ISSN 10876596, Glass Physics and Chemistry, 2013, Vol. 39, No. 3, pp. 248–260
8. G.A. Khater, Influence of Cr_2O_3 , LiF , CaF_2 and TiO_2 nucleants on the crystallization behavior and microstructure of glass-ceramics based on blast-furnace slag, *Ceramics International* 37 (2011) pp.2193–2199.
9. Zhong-jie Wang, Wen Ni, Yan Jia, Li-ping Zhu, Xiao-yan Huang, Crystallization behavior of glass ceramics prepared from the mixture of nickel slag, blast furnace slag and quartz sand, *Journal of Non-Crystalline Solids* 356 (2010) pp.1554–1558.